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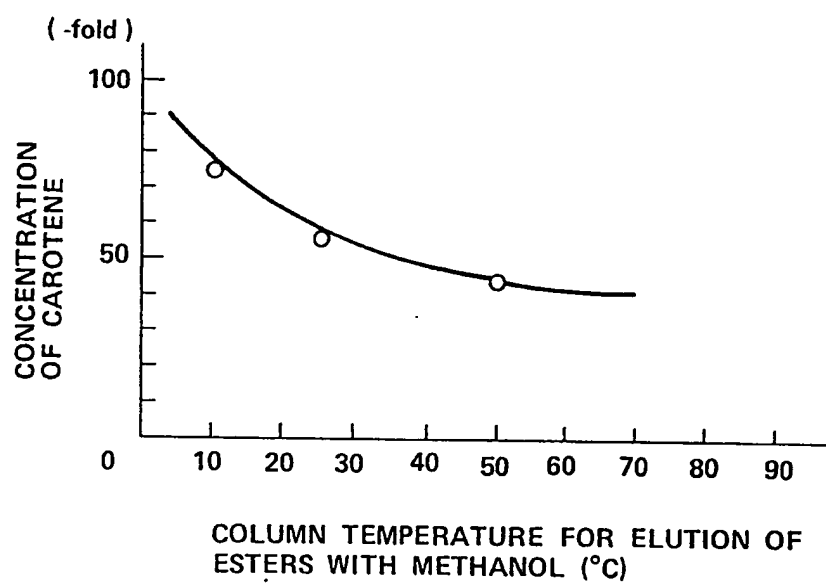
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**(54) A process for producing carotene from oils and fats**

(57) A process for producing carotene comprises subjecting carotene-containing natural oils and fats to alcoholysis with a lower monoalcohol, collecting the oil phase containing carotene and consisting mainly of fatty acid lower alkyl esters, mixing the oil phase with a hydrophilic solvent and water to cause carotene to separate out, and collecting the thus separated carotene. The carotene layer may be adsorbed onto styrene/divinyl benzene copolymer washed with alcohol to remove any esters and then eluting the carotene with a hydrophobic solvent such as hexane.

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## SPECIFICATION

## Process for treating natural oils and fats

5 This invention relates to a process for treating natural oils and fats to recover efficiently trace amounts of carotene contained therein.

It is known that carotene which is a carotenoid hydrocarbon is useful as a provitamin A or as an edible dye. Carotene can be obtained by synthesis and it can also be obtained by recovering trace amounts contained in natural oils and fats. According to the conventional process for recovering carotene from natural oils and fats, carotene-  
10 containing natural oils and fats are saponified and then carotene remaining unsaponified is extracted with a solvent, or carotene-containing natural oils and fats undergo alcoholysis with a lower alcohol to give fatty acid lower alkyl esters, which are then  
15 distilled away under reduced pressure, whereby carotene is concentrated in the distillation residues.

The former process by solvent extraction is poor in efficiency of carotene recovery and a large amount of solvent is necessary if carotene is to be recovered  
20 in high yields. This leads to a high production cost. Moreover, the oils and fats left after the recovery of carotene become colored soap which does not readily find effective use. The latter process by distillation under reduced pressure has to be per-  
25 formed at a low temperature under a high vacuum so that the decomposition of carotene is prevented. This requires high equipment cost and operating cost and, in turn, leads to a high production cost.

An object of this invention is to provide a process  
30 for treating natural oils and fats to recover trace amounts of carotene contained therein in high yields in the concentrated form with a low cost.

As the result of an intensive study on the process for recovering carotene efficiently from natural oils  
35 and fats in high yields and in high concentrations, the present inventors have found that the object can be achieved by subjecting carotene-containing natural oils and fats to alcoholysis with a lower monoalcohol, collecting the oil phase containing carotene  
40 and consisting mainly of fatty acid lower alkyl esters, mixing the oil phase with a hydrophilic solvent and water to cause carotene to separate out, and collecting thus separated carotene.

According to the process of this invention, natural  
45 oils and fats containing carotene are subjected to alcoholysis with a lower monoalcohol to give an oil phase which contains carotene and consists mainly of fatty acid lower alkyl esters. To this oil phase is added a hydrophilic solvent and water. This reduces  
50 the solubility of hydrophobic carotene and fatty acid lower alkyl esters in the hydrophilic solvent. Thus, the solution separates into two layers, one containing carotene and a small amount of fatty acid lower alkyl esters, and the other containing a large amount  
55 of fatty acid lower alkyl esters, hydrophilic solvent, and water. The layer containing carotene in high concentrations is collected. In the case where the step of collecting the carotene layer is performed at 30 to 70°C, and then the remaining layer of hydrophilic solvent is cooled at 10 to 30°C, the fatty acid lower

alkyl esters can be separated and collected. At the same time the hydrophilic solvent is collected, which is recycled.

The collected carotene layer may preferably be  
60 brought into contact with styrene-divinylbenzene copolymer resin to adsorb carotene and the residual esters in the carotene layer on the copolymer resin. Then, the copolymer resin is brought into contact with a lower monoalcohol such as methanol and  
65 ethanol to dissolve the esters on the resin into the lower monoalcohol and leave the carotene adsorbed on the resin. After the esters are eluted with the lower monoalcohol from the resin, the resin is brought into contact with a hydrophobic solvent to  
70 dissolve the carotene on the resin into the solvent and elute the carotene with the solvent from the resin. The eluted carotene is highly concentrated.

According to the present invention, it is possible to recover carotene in high yields in the concentrated  
75 form from natural oils and fats containing trace amounts of carotene, using a simple apparatus and process. In addition, the process of this invention provides as a by-product purified, discolored fatty acid lower alkyl esters.

80 The following is the detailed description of the present invention with reference to an accompanying drawing, in which:

the drawing is a graph showing a relationship between column temperatures in the step of elution  
85 of esters with methanol and concentrations of carotene in the case that a carotene-containing fatty acid lower alkyl ester is brought into contact with styrene-divinylbenzene copolymer resin in a column to concentrate carotene.

90 The process of this invention starts with subjecting carotene-containing natural oils and fats to alcoholysis with a lower monoalcohol, and then collecting the oil phase containing carotene and consisting mainly of fatty acid lower alkyl esters. More detailed-  
95 ly, carotene-containing natural oils and fats are incorporated with a lower monoalcohol such as methanol and ethanol, whereby the glyceride in the natural oils and fats is converted through alcoholysis into glycerin and lower alkyl esters of higher fatty acids. Carotene in the oils and fats is contained,  
100 along with the unreacted glyceride, in the alkyl ester phase (oil phase). The oil phase is separated from glycerin by standing or centrifuging. The carotene-containing natural oils and fats that can be treated according to the process of this invention are not specifically limited. A preferred example is palm oil.

In the subsequent step, the oil phase containing carotene and consisting mainly of fatty acid lower alkyl esters is mixed with a hydrophilic solvent and  
105 water to cause carotene to separate out. The layer containing carotene in high concentrations is collected by standing or centrifuging.

There are no specific limitations in method and order of mixing the oil phase with a hydrophilic solvent and water. Preferably, the oil phase is dissolved in a hydrophilic solvent and then water is added to the resulting solution so that carotene is caused to separate out.

There are no specific limitations in the type of  
110 hydrophilic solvent. Preferred examples include

methanol, ethanol, isopropanol, and acetone. They may be used individually or in combination with one another. The hydrophilic solvent may preferably be added so that the concentration of fatty acid lower alkyl esters is 5 to 20% by weight of the hydrophilic solvent. Where methanol or ethanol is used as the hydrophilic solvent, carotene separates out in the lower layer, and where isopropanol or acetone is used as the hydrophilic solvent, carotene separates out in the upper layer.

The amount of water may preferably be 1 to 20% by weight of the hydrophilic solvent. This step may be performed at 10 to 70°C. The carotene layer thus separated contains carotene, and a portion of fatty acid lower alkyl ester and the hydrophilic solvent. Thus the solvent may preferably be distilled away in the usual way so that a concentrate of carotene is obtained.

The layer of the hydrophilic solvent which is left after the collection of the carotene layer mainly contains fatty acid lower alkyl esters with little carotene. After the removal of the hydrophilic solvent, there is recovered discolored fatty acid lower alkyl esters. Upon simple purification treatment, they can be made into a good quality raw material for higher fatty acids and surface active agents.

As mentioned above, the oil phase containing carotene and consisting mainly of fatty acid lower alkyl esters is mixed with a hydrophilic solvent and water to cause carotene to separate out. This step may preferably be performed at 30 to 70°C. After the layer containing carotene in high concentrations has been collected, the remaining hydrophilic solvent layer is replenished with the same hydrophilic solvent, if necessary. This step may preferably be performed at 10 to 30°C so that the separation of fatty acid lower alkyl esters containing little carotene can be performed efficiently. Thus the fatty acid lower alkyl esters are collected, and at the same time, the hydrophilic solvent and water are collected.

There should be a great temperature difference between the first step in which the layer containing carotene in high concentrations is collected and the second step in which the fatty acid lower alkyl esters are collected. In practice, the preferred temperature difference is 20 to 40°C. The hydrophilic solvent and water which have been recovered in this way contain a small amount of fatty acid lower alkyl esters and carotene; the recovered solvent can be recycled for use as the solvent for separating carotene without the removal of the esters and carotene contained therein.

The carotene-concentrated layer collected as mentioned above may further be brought into contact with styrene-divinylbenzene copolymer resin, as such or after the removal of water and the hydrophilic solvent remained therein, whereby carotene and residual esters are adsorbed on the copolymer resin. Then the copolymer resin is brought into contact with a lower monoalcohol so that the esters are dissolved in the lower monoalcohol. Finally, the copolymer resin is brought into contact with a hydrophobic solvent so that carotene is dissolved in the solvent. In this way, the concentration of carotene is further increased.

When carotene and the fatty acid lower alkyl esters are brought into contact with styrene-divinylbenzene copolymer resin, carotene and the esters readily adsorb onto the copolymer resin because of its high adsorptive affinity for hydrophobic substances. Subsequently, the copolymer resin is brought into contact with a lower monoalcohol in which carotene is difficultly soluble, whereby the esters alone are dissolved in the lower monoalcohol. After the separation of the esters, the copolymer resin is brought into contact with a hydrophobic solvent such as hexane, chloroform, and petroleum ether in which carotene is readily soluble. In this way, carotene alone is dissolved in the solvent, and the solution containing carotene in high concentrations is obtained.

There are no specific limitations in the shape of the styrene-divinylbenzene copolymer resin, although the one in the form of powder or granule is preferable.

There are also no specific limitations in the method of bringing the carotene-concentrated layer to the styrene-divinylbenzene copolymer resin. Contacting may be accomplished by using a column or batchwise. The column method is preferable from the standpoint of efficient adsorption of carotene. The carotene-concentrated layer of 0.2 to 0.5 g per ml of the resin filled in the column may preferably be passed through the column. If the load is in excess of 0.5 g/ml-resin, the resin may become saturated readily and permit carotene to pass unadsorbed.

The contacting of the carotene-concentrated layer with the styrene-divinylbenzene copolymer resin can be performed more efficiently if the layer is previously diluted with a lower monoalcohol which is used for the elution of esters mentioned later.

Styrene-divinylbenzene copolymer resin adsorbs hydrophobic substances more readily than hydrophilic substances. Because of this characteristic property, it adsorbs carotene, esters, and alcohol in the order mentioned.

The copolymer resin which has adsorbed the carotene-concentrated layer is then brought into contact with a lower monoalcohol, preferably a C<sub>1</sub>-C<sub>4</sub> lower monoalcohol, in which carotene is not soluble. In this way, the alcohol-soluble esters in the carotene-concentrated layer are dissolved in the alcohol. In this step, carotene remains adsorbed on the resin. Preferred lower monoalcohols are methanol and ethanol. The lower monoalcohols may be used individually or in combination with one another. For the elution of esters, the lower monoalcohol may be used in an amount of 1 to 5 times the volume of the resin.

After separation of the esters, the copolymer resin is brought into contact with a hydrophobic solvent in which carotene is readily soluble, whereby carotene is eluted in the solvent and the eluate is collected.

There are no specific restrictions in the type of the hydrophobic solvent in which carotene is readily soluble. Preferred examples are hexane, chloroform, and petroleum ether. They may be used individually or in combination with one another. Hexane is particularly preferable from the standpoint of safety in the case where recovered carotene is used for

foods, .g., as an edible dye.

For elution of carotene, the hydrophobic solvent may be used in an amount of 0.5 to 2 times the volume of the resin. This makes it possible to elute almost completely the adsorbed carotene.

Where the above-mentioned step is performed with a column, the column temperature may be kept at 0 to 80°C, preferably 0 to 20°C, for the adsorption of carotene concentrated layer and the elution of esters with a lower monoalcohol. At these temperatures, the adsorption of carotene increases, and hence the ratio of concentration increases. The column temperature in the step of eluting carotene with a hydrophobic solvent may be any temperature lower than the boiling point of the hydrophobic solvent. The resin from which carotene has been removed can be used repeatedly if the hydrophobic solvent remaining on the resin is replaced by the alcohol for the elution of esters.

The carotene which has been separated from the resin and collected may be used as such without removal of the hydrophobic solvent, depending on uses. Preferably, the solvent should be distilled away in the usual way.

The fatty acid lower alkyl esters which have been eluted from the resin can also be recycled as such.

As mentioned above, the process of the invention comprises the steps of subjecting carotene-containing natural oils and fats to alcoholysis with a lower monoalcohol, collecting the oil phase containing carotene and consisting mainly of fatty acid lower alkyl esters, mixing the oil phase with a hydrophilic solvent and water to cause carotene to separate out, and collecting thus separated carotene.

This process makes it possible to concentrate and recover in a simple manner the carotene in natural oils and fats which is almost entirely decomposed and discarded without being effectively used in the case where the conventional purification process is employed. The process of this invention does not include any high-temperature step and hence recovers carotene in high yields without loss due to decomposition of carotene. In addition, it affords as a by-product fatty acid lower alkyl esters, with carotene removed.

In a preferred embodiment of the process, the oil phase containing carotene and consisting mainly of fatty acid lower alkyl esters is mixed with a hydrophilic solvent and water at 30 to 70°C, whereby the carotene-concentrated layer is collected. The remaining hydrophilic solvent layer is cooled to 10 to 30°C to cause the fatty acid lower alkyl esters to separate out. The esters are collected and, at the same time, the hydrophilic solvent is collected, which is recycled. The recovery of the hydrophilic solvent in this way requires only a small amount of heat as compared with the recovery of the hydrophilic solvent by distillation. The recovered solvent can be used repeatedly for the elution of carotene after replenishment of lost solvent and water (about one-tenth of the amount of the oil phase). Thus the process of this invention is very economical from the standpoint of energy saving.

The concentration of carotene is highly increased by contacting the above-said carotene-concentrated

layer with styrene-divinylbenzene copolymer resin to adsorb carotene and the residual esters on the resin, eluting the ester with a lower monoalcohol from the resin, and eluting carotene with a hydrophobic solvent to collect the eluted carotene.

The invention is described in more detail with reference to the following examples.

#### Example 1

Thirty grams of crude palm oil containing 620 ppm of carotene was subjected to methyl esterification by adding 10 g of methanol and 0.24 g of sodium hydroxide. The resulting ester layer was collected and washed with 5 g of water, followed by dehydration in the usual way. The ester layer was then uniformly dissolved in 210 g of methanol and 8.5 g of water was added to the methanol solution, followed by standing at 20°C for 1 hour. The lower layer in which carotene had separated out was collected.

Residual trace amounts of methanol and water were removed. Thus there was obtained 5.8 g of concentrate containing 2720 ppm of carotene. (Concentration of carotene: 4.4-fold, recovery of carotene: 84.8%)

After removal of methanol and water from the upper layer, there was obtained 23.3 g of discolored ester containing 97 ppm of carotene.

The above-mentioned concentrate (5.8 g) containing 2720 ppm of carotene was mixed with 40 g of methanol and 1.5 g of water, followed by standing. After removal of methanol and water from the lower layer, there was obtained 1.2 g of concentrate containing 1.1% of carotene.

#### Example 2

Thirty grams of crude palm oil containing 583 ppm of carotene was treated in the same manner as in Example 1. The resulting ester layer was dissolved in 450 g of methanol and 45 g of water was added to the methanol solution, followed by standing at 60°C for 1 hour. The lower layer in which carotene had separated out was collected, and residual trace amounts of methanol and water were removed. Thus there was obtained 5.5 g of concentrate containing 2500 ppm of carotene. (Concentration of carotene: 4.3-fold, recovery of carotene: 78.6%)

When the upper layer was cooled to 20°C and followed to stand, 7 g of discolored ester containing 150 ppm of carotene separated out. After collecting the discolored ester, there were recovered 447 g of methanol, 44 g of water, and 14.7 g of fatty acid lower alkyl ester containing 63 ppm of carotene. The thus obtained methanol solution could repeatedly be used for the elution of carotene.

#### Example 3

Thirty grams of crude palm oil containing 518 ppm of carotene was treated in the same manner as in Example 1. The resulting ester layer was uniformly dissolved in 200 g of ethanol, and to the solution was added 54 g of water, followed by standing at 20°C for 1 hour. The lower layer in which carotene had separated out was collected, and residual trace amounts of ethanol and water were removed. Thus there was obtained 8.0 g of concentrate containing

1400 ppm of carotene. (Concentration of carotene: 2.7-fold, recovery of carotene: 72.1%)

After removal of ethanol and water from the upper layer, there was obtained 21.0 g of discolored ester containing 175 ppm of carotene.

#### Example 4

Thirty grams of crude palm oil containing 530 ppm of carotene was treated in the same manner as in Example 1. The resulting ester layer was uniformly dissolved in 200 g of isopropanol, and to the solution was added 147 g of water, followed by standing at 20°C for 1 hour. The upper layer in which carotene had separated out was collected, and residual trace amounts of isopropanol and water were removed. Thus there was obtained 16.8 g of concentrate containing 866 ppm of carotene. (Concentration of carotene: 1.6-fold, recovery of carotene: 90.9%)

#### Example 5

Thirty grams of crude palm oil containing 600 ppm of carotene was treated in the same manner as in Example 1. The resulting ester layer was uniformly dissolved in 200 g of acetone, and to the solution was added 45 g of water, followed by standing at 20°C for 1 hour. The upper layer in which carotene had separated out was collected, and residual trace amounts of acetone and water were removed. Thus there was obtained 14.8 g of concentrated containing 990 ppm of carotene. (Concentration of carotene: 1.7-fold, recovery of carotene: 81.4%)

#### Example 6

Thirty grams of crude palm oil containing 670 ppm of carotene was treated in the same manner as in Example 1. To the resulting ester layer was added 220 g of methanol solution containing 4% by weight of water. After thorough mixing, the solution was centrifuged at 20°C. The lower layer was collected and dehydrated. It was passed through a column filled with 20 ml of styrene-divinylbenzene copolymer resin powder at 20°C. The esters were eluted and separated by passing 100 ml of methanol through the column at a space velocity of  $3.5 \text{ hr}^{-1}$ . Then 30 ml of hexane was passed through the column to elute and separate carotene. After distillation of hexane from the eluate, there was obtained 0.12 g of concentrate containing 13.2% of carotene. (Concentration of carotene: 197-fold, recovery of carotene: 78.8%)

#### Referential Example

Thirty grams of crude palm oil containing 620 ppm of carotene was subjected to methyl esterification by adding 10 g of methanol and 0.24 g of sodium hydroxide. The resulting ester layer was collected and washed with 5 g of water. The ester was dissolved in 100 ml of methanol. The ester solution in methanol was passed through a column filled with 100 ml of styrene-divinylbenzene copolymer resin powder at 20°C, so that the resin adsorbs carotene, methyl ester of palm oil, and unreacted palm oil. The ester and unreacted palm oil were eluted and separated by passing 200 ml of methanol through the column at a space velocity of  $2 \text{ hr}^{-1}$ . Then 100 ml

of n-hexane was passed through the column to elute and separate carotene. After distillation of hexane from the eluate, there was obtained 0.35 g of concentrate containing 3.9% of carotene. (Concentration of carotene: 63-fold, recovery of carotene: 73%)

The above-mentioned experiment was performed at different column temperatures for elution of esters with methanol. The results are shown in the accompanying drawing in which the concentration of carotene is plotted against the column temperature.

#### CLAIMS

1. A process for treating natural oils and fats which comprises subjecting carotene-containing natural oils and fats to alcoholysis with a lower monoalcohol, collecting the oil phase containing carotene and consisting mainly of fatty acid lower alkyl esters, mixing the oil phase with a hydrophilic solvent and water to cause carotene to separate out, and collecting thus separated carotene layer.
2. A process according to Claim 1, wherein the hydrophilic solvent is a single or mixed solvent selected from methanol, ethanol, isopropanol, and acetone.
3. A process according to Claim 1 or Claim 2, wherein the oil phase containing carotene and consisting mainly of fatty acid lower alkyl esters is mixed with a hydrophilic solvent and water at 10 to 70°C.
4. A process according to any one of Claims 1 to 3, wherein the oil phase containing carotene and consisting mainly of fatty acid lower alkyl esters is mixed with a hydrophilic solvent and water to cause carotene to separate out, and after the separated carotene layer is collected, the hydrophilic solvent and water are removed from the remaining hydrophilic solvent layer and the fatty acid lower alkyl esters are collected.
5. A process according to Claim 4, wherein the oil phase containing carotene and consisting mainly of fatty acid lower alkyl esters is mixed with a hydrophilic solvent and water at 30 to 70°C to cause carotene to separate out, and after the separated carotene layer is collected, the remaining hydrophilic solvent layer is cooled to 10 to 30°C to cause the fatty acid lower alkyl esters to separate out from the hydrophilic solvent and water and the thus separated esters are collected.
6. A process according to any one of Claims 1 to 5, wherein the collected carotene layer is brought into contact with styrene-divinylbenzene copolymer resin to adsorb carotene and the residual esters on the resin, the resin is brought into contact with a lower monoalcohol to elute the esters with the lower monoalcohol from the resin, and thereafter the resin is brought into contact with a hydrophobic solvent to elute carotene with the solvent from the resin and collect it, whereby carotene is further concentrated.
7. A process according to Claim 6, wherein the lower monoalcohol is a single or mixed alcohol selected from a  $C_1$ - $C_4$  lower monoalcohol.
8. A process according to Claim 6, wherein the

hydrophobic solvent is a single or mixed solvent selected from hexane, chloroform and petroleum ether.

9. A process according to any one of Claims 6 to 8, wherein the adsorption of the carotene layer and the elution of the esters is carried out at a temperature of 0 to 80°C.

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